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Fluorination with Xenon Difluoride. Fluorine Addition to 1-Phenylacetylenes

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Electrophilic addition of halogens to olefinic systems has been the subject of considerable study.[1] The analogous additions[1,2] to acetylenic systems have received much less attention. In particular, the addition of molecular fluorine,[3] chlorine monofluoride,[4] bromine monofluoride,[4,5] and iodine monofluoride[4] to acetylenes has been studied. Our recent observations that xenon difluoride adds fluorine to 1-aryl-substituted olefins[6,7] and the phenanthrene system[8] to form vicinal difluorides led us to investigate the fluorine addition to carbon–carbon triple bond with this reagent.

Although there is a structural relationship between carbon–carbon double bonds and triple bonds, the reactivities of the two systems toward electrophilic reagents are quite different. In a very recent work,[9] the rate ratio $k_{\mathrm{olefin}}/k_{\mathrm{acetylene}}$ of the order of 10^5 in bromination and chlorination of styrene–phenylacetylene and other olefin–acetylene pairs was observed. This difference was explained in terms of different ease of formation of carbonium ions and vinyl cations in electrophilic additions. In view of this consideration it was not certain that XeF_2 would add fluorine to 1-phenylacetylenes at all. Recently, propyne[10] was found to be resistant to fluorine addition with XeF_2 in a gas-phase reaction. After 100 days at room temperature it gave 2,2-difluoropropane in a 33% yield and at least nine other trace products. On the other hand, the addition across the triple bond might undergo accompanying substitution of the phenyl ring if one takes into account the ease of fluorination of benzene derivatives[11] with XeF_2. Therefore a study was undertaken to establish these points.

The fluorine additions to acetylenes (1) with xenon difluoride were conducted at 25° in methylene chloride with anhydrous hydrogen fluoride as catalyst. Less than stoichiometric amounts of xenon difluoride did not favor difluoro olefin formation and only tetrafluoride (2) and unreacted acetylene were found in the reaction mixture. However, the use of 2.5 equiv of XeF_2 led to the formation of 2 in over 50% yield.

$$\underset{\mathbf{1}}{\mathrm{PhC{\equiv}CR}} + 2\mathrm{XeF_2} \xrightarrow[\mathrm{CH_2Cl_2}]{\mathrm{HF}} \underset{\mathbf{2}}{\mathrm{PhCF_2CF_2R}} + 2\mathrm{Xe}$$

a, R = Ph
b, R = CH_3
c, R = n-C_3H_7

The structures of previously known **2a**[3] and **2b**[3] were identified and that of unknown **2c** assigned by its ir, ^1H and ^{19}F nmr, and mass spectra.

The acetylenes seem to fluorinate completely to tetrafluoride, which implies that difluoro olefin is more reactive for fluorine addition than is the parent acetylene. The same results were found in molecular fluorine addition[3] to acetylenes at low temperature. We also observed the facile fluorine addition to 9,10-difluorophenanthrene[8] with XeF_2, yielding 9,9,10,10-tetrafluoro-9,10-dihydrophenanthrene as the reaction product.

One anomalous reaction was noted in this series of experiments. Phenylacetylene did not give 1,1,2,2-tetrafluoro-1-phenylethane, the expected product. Instead, some polymeric material was formed in this reaction.

The fluorine addition to acetylenes with XeF_2 appears to be strongly catalyzed by HF, as indicated by observation that in the absence of this catalyst reactions are very slow. We found evidence neither for the formation of fluorine-substituted products which might arise *via* a substitution fluorination of the phenyl ring nor for the presence of HF addition products, observed in the gas-phase fluorinations[10] with XeF_2. Extensive work is in progress on acid-catalyzed liquid—phase fluorination of various acetylenic systems with this reagent, which appears to be useful also for applications on a large scale.

Experimental Section[12]

Materials. The acetylenes were obtained from commercial sources and purified by vpc to conform with published physical and spectral data. Xenon difluoride was prepared by the photosynthetic method[13] and its purity was better than 99.5%. Methylene chloride was purified by the method[14] and stored over molecular sieves. Hydrogen fluoride of Fluka purum quality was used.

1,1,2,2-Tetrafluoro-1,2-diphenylethane (2a). To a solution of **1a** (0.178 g, 1.0 mmol) in methylene chloride (6 ml), xenon difluoride (0.423 g, 2.5 mmol) was added at 25° and under stirring anhydrous HF (0.100 g, 5.0 mmol) was introduced into the reaction mixture. After a few seconds the colorless solution turned dark blue and xenon gas was slowly evolved. After 6 hr gas evolution had ceased and the reaction appeared to be complete. The reaction mixture was diluted with methylene chloride (15 ml), washed (10 ml of 5% aqueous $NaHCO_3$), and dried (Na_2SO_4), and solvent was evaporated *in vacuo*. The crude product was sublimated (50°, 0.1 mm) to give **2a:** mp 121–122° (lit.[3] mp 119.3–120.5°); yield 0.163 g (64%); mass spectrum m/e 254 (M^+).

1,1,2,2-Tetrafluoro-1-phenylpropane (2b). To a solution of **1b** (0.116 g, 1.0 mmol) in methylene chloride (5 ml), xenon difluoride (0.338 g, 2 mmol) was added at 25° and under stirring anhydrous HF (0.02 g, 1 mmol) was introduced into the reaction mixture. After a few seconds the colorless solution turned dark blue and xenon gas was evolved slowly. After 6 hr, the reaction mixture was diluted with methylene chloride (15 ml), washed (10 ml of 5% aqueous $NaHCO_3$), and dried (Na_2SO_4), and solvent was evaporated *in vacuo*. The crude oily product was purified by vpc (6 × 0.25 in. SE-30 10% on Chromosorb A, 160°) to give **2b** as a colorless, stable liquid, yield 0.102 g (53%); mass spectrum m/e 192 (M^+); nmr (CCl_4) δ 1.75 (tt, 3 H, $-CH_3$, J = 19 Hz, $-CF_2CH_3$, J = 1 Hz, $-CF_2CF_2CH_3$), 7.35 (m, 5 H, Ph).

1,1,2,2-Tetrafluoro-1-phenylpentane (2c). The fluorination, work-up procedure and vpc purification were essentially the same as described for **2b**. **2c** was a colorless stable liquid: yield 0.122 g (55%); high-resolution mass spectrum m/e 144.0931 ($M - 4F)^+$ (calcd for $C_{11}H_{12}$, 144,0934); nmr (CCl_4) δ 0.93 (t, 3 H, $-CH_3$), 1.8 (m, 4 H, $-CH_2CH_2-$), 7.26 (m, 5 H, Ph), −125.0 (m, $PhCF_2-$), −127.8 (m, $-CF_2C_3H_7$).

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Registry No.—**1a,** 501-65-5; **1b,** 673-32-5; **1c,** 4250-81-1; **2a,** 425-32-1; **2b,** 14210-87-8; **2c,** 51821-09-1; XeF_2, 13709-36-9.

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Selective Cleavage of β-Keto Esters by 1,4-Diazabicyclo[2.2.2]octane (Dabco)

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As a result of a continuing study utilizing nitrogenous bases,[1-4] we now wish to report that 1,4-diazabicyclo[2.2.2]octane (Dabco) is useful for the cleavage of β-keto esters.

β-Keto ester 1 was treated with 6 equiv of Dabco in 16 equiv of *o*-xylene at reflux (165°) for 6 hr to give ketone **10** as a white, crystalline solid in 84% yield. Ketone **10** was identical by ir, nmr, mass spectrum, glc retention time, and mixture melting point with an authentic sample prepared from 1 by a known procedure.[5]

The generality of Dabco as a reagent for cleaving β-keto esters is demonstrated by the results illustrated in Scheme I. Typically, a mixture of 1 equiv of the appropriate β-keto ester and 10 equiv of Dabco in 15 equiv of *o*-xylene was heated to reflux for 4 hr.[11] The resulting ketones (**11–14**) were obtained in greater than 96% yield by glc analyses and were identical by mass spectral and glc retention time comparison with authentic samples.[5,8]

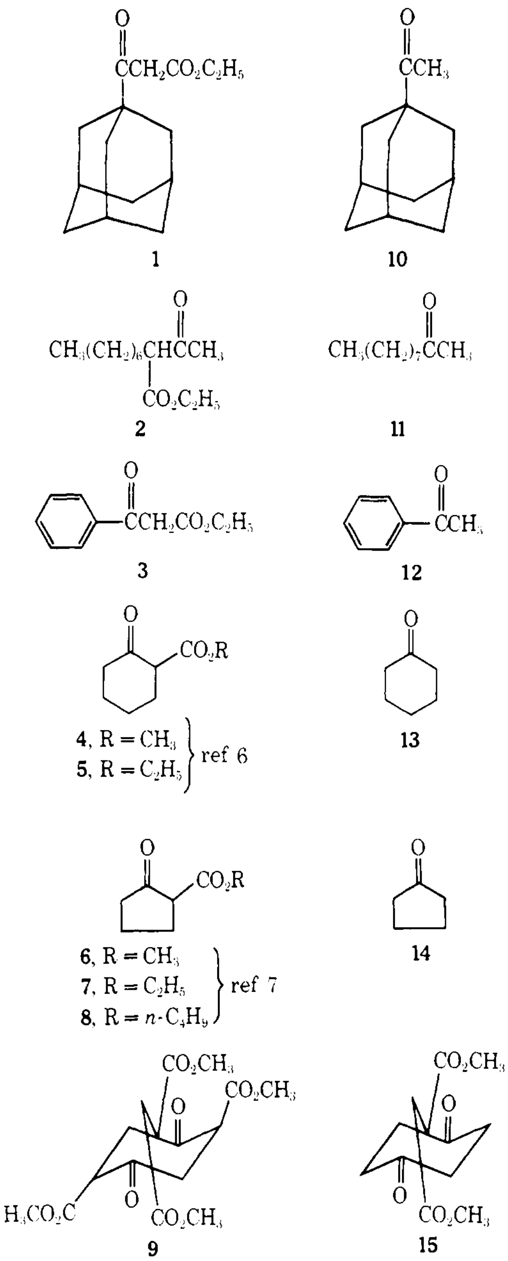
The selectivity of the cleavage reaction is demonstrated by the application of Dabco to the cleavage of substrate **9** to give compound **15**. This result shows that only the β-keto esters with at least one α hydrogen were cleaved. The report[4] that a variety of nonconjugated esters are stable under conditions similar to those which cleaved β-keto esters provides further evidence of selectivity.

The facile cleavage of methyl, ethyl, and *n*-butyl β-keto esters with a reagent (Dabco) that does not cleave saturated esters by either the *O*-alkyl cleavage or hydrolytic routes suggests that a mechanism similar to that reported by Krapcho and Lovey[5,12] for the cleavage of β-keto esters with sodium chloride and DMSO is probably operative.

A variety of reagents have been reported for achieving the cleavage of β-keto esters.[5,9] However, to our knowledge this is the first report involving the utilization of a nonionic reagent in a relatively nonpolar solvent system.

Experimental Section

Scheme I



Infrared spectra were obtained using a Perkin-Elmer Model 137G spectrophotometer. Nuclear magnetic resonance spectra were obtained using a Jeolco Minimar spectrometer. Tetramethylsilane was used as an internal standard. Mass spectra were obtained using a Perkin-Elmer Model 270 mass spectrometer. Gas-liquid chromatography (glc) was performed using a Hewlett-Packard Model 402 gas chromatograph with a hydrogen flame detector. A glass column (6 ft × 3 mm i.d.) packed with 5% SE-30 on 80/100 mesh Chromosorb W (programed from 70 or 100° to 200° at 5°/min) with a nitrogen flow rate of 11 ml/min was used for the glc analyses of most compounds. A metal column (6 ft × 2 mm i.d.) packed with 4% SE-30 and 6% QF-1 on 80/100 mesh Chromosorb W (programed from 100 to 200° at 5°/min) with a nitrogen flow rate of 10 ml/min was used for the glc analyses of compounds **3** and **12**. A glass column (6 ft × 3 mm i.d.) packed with 5% Apiezon L on 80/100 mesh Chromosorb W (programed from 62 to 200° at 5°/min) with a flow rate of 10 ml/min was used for the glc analyses of compounds **4**, **5**, and **13**. Melting points were obtained on a Fisher-Johns apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Decarbethoxylation of β-Keto Ester 1. A mixture of β-keto ester 1 (2.239 g, 9.9 mmol) and Dabco (5.926 g, 52.9 mmol) in *o*-xylene (14.639 g, 138.1 mmol) was heated to reflux for 6 hr in an oil bath with constant stirring. The ether extract of the acidified (0.6 *M* HCl) reaction mixture was washed with water, dried over anhydrous $MgSO_4$, and evaporated *in vacuo*. The crude product was purified through a column packed with silica gel alumina and recrystallized from methanol to give 1.289 g (84%) of white, crystalline **10**: mp 55.5–56.5° (lit.[10] mp 53–54°); λ_{max} (KBr) 2780, 1670, 1430, 1330, 1240 cm^{-1}; nmr ($CDCl_3$) δ 1.77 (15 H, multiplet), 2.07 (3 H);